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(51)Int.Cl.

**H01M 8/02****H01M 8/10**(21)Application number : **05-067646**(71)Applicant : **ASAHI GLASS CO LTD**(22)Date of filing : **03.03.1993**(72)Inventor : **TAMURA MASAYUKI  
JITSUKATA KIYOSHIGE  
MIYAKE HARUHISA****(54) FUEL CELL WITH SOLID HIGHPOLYMER ELECTROLYTE**

(57)Abstract:

PURPOSE: To provide a high performance fuel cell which uses a solid high- polymer electrolyte having a low electric resistance.

CONSTITUTION: The solid electrolyte used consists of a positive ion exchange film which is made from a perfluorocarbon polymeride film having an AC specific resistance value of  $5 \cdot 10^{-11} \Omega \cdot \text{cm}$ .

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CLAIMS

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[Claim(s)]

[Claim 1] The solid-state polyelectrolyte type fuel cell characterized by having the current-ratio resistance whose above-mentioned cation exchange membrane is 5-11-ohmcm in the fuel cell which uses as a solid-state polyelectrolyte type the cation exchange membrane which consists of a perfluoro carbon polymer which has a sulfonic group.

[Claim 2] The solid-state polyelectrolyte type fuel cell of the claim 1 whose thickness of a cation exchange membrane is 30-300 micrometers.

[Claim 3] A perfluoro carbon polymer is  $\text{CF}_2=\text{CF}_2$ . The claim 1 or 2 solid-state polyelectrolyte type fuel cells which consist of a copolymer with  $\text{CF}_2=\text{CF}(\text{OCF}_2\text{CFX})_m\text{Oq}(\text{CF}_2)_n\text{A}$  (inside of a formula  $m=0-3$ ,  $n=0-12$ ,  $q=0$  or  $1$ ,  $X=\text{F}$  or  $\text{CF}_3$ ,  $\text{A}=\text{sulfonic-acid type functional group}$ ).

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to a solid-state polyelectrolyte type fuel cell.

[0002]

[Description of the Prior Art] Research of the fuel cell (solid-state polyelectrolyte type fuel cell) using the poly membrane of proton conductivity as an electrolyte is progressing in recent years. A solid-state polyelectrolyte type fuel cell operates at low temperature, has the feature that power density can be high and can be miniaturized, and is seen as a hopeful to uses, such as a power supply for mount.

[0003]

[Problem(s) to be Solved by the Invention] The poly membrane used for the above-mentioned use excels [ cation exchange membrane / which consists of a perfluoro carbon polymer which proton conductivity ion exchange membrane with a thickness of 100-200 micrometers is usually used, and has especially a sulfonic group ] in a basic property, and it inquires widely. However, the electric resistance of the cation exchange membrane proposed now cannot say that it is low not necessarily enough from a viewpoint which obtains the cell of high power density more.

[0004] Although the method of reducing the electric resistance of a cation exchange membrane has the increase in sulfonic group concentration, and reduction of thickness, the remarkable increase in sulfonic group concentration reduces a membranous mechanical strength, or in long-term operation, a film becomes easy to carry out the creep of it, and the problem of reducing endurance produces it. On the other hand, reduction of thickness reduces a membranous mechanical strength, or the problem of reducing processability and handling nature, such as junction to a gas diffusion electrode, further produces it. In this way, development of a cation exchange membrane with a high mechanical strength with low and electric resistance was desired.

[0005]

[Means for Solving the Problem] this invention is made that the above-mentioned \*\*\*\* should be solved, and the solid-state polyelectrolyte type fuel cell characterized by having the current-ratio resistance whose cation exchange membrane is 5-11-ohmcm is offered in the fuel cell which makes the cation exchange membrane of the perfluoro carbon polymer containing a sulfonic group a solid-state polyelectrolyte.

[0006] By this invention, the current-ratio resistance of a cation exchange membrane is measured about the cation exchange membrane (an ion exchange group is an acid type) immersed at 25 degrees C into the sulfuric-acid solution of 1M for 24 hours, and is computed like several 1.

[0007]

[Equation 1] Current-ratio resistance (omegacm) = resistance (omega) x film effective-area (cm<sup>2</sup>) / thickness (cm)

[0008] Since a membrane resistance goes up by this invention when the current-ratio resistance of a cation exchange membrane is larger than the above-mentioned upper limit, the output of a cell declines, and film intensity and film handling nature fall on the other hand in being smaller than a lower limit, it is not desirable. Especially current-ratio resistance has desirable 6-10-ohmcm especially.

[0009] Carrying out a membranous degree of swelling to 50 - 90% of the weight in the hydrolysis processing which introduces an ion exchange group as a method of cheating out of the current-ratio resistance of a cation exchange membrane in the above-mentioned range by this invention, \*\*\*\*ing a degree of swelling to 65 - 110% of the weight by boiling or pressurizing and warming a cation exchange membrane in pure water, etc. can adopt preferably.

[0010] Although the cation exchange membrane of a perfluoro carbon polymer consists of a film of a monolayer preferably, the thickness has [ making it be 30-300 micrometers and further 50-250 micrometers ] a desirable thing. Since the handling nature in film intensity, electrode junction, etc. falls, a membrane resistance goes up and the output of a cell declines on the other hand when larger than a upper limit in being smaller than the above-mentioned lower limit, it is not desirable.

[0011] As a perfluoro carbon polymer containing the sulfonic group used for this invention, a copolymer with the fluoro vinyl compound expressed with a tetrafluoroethylene and CF<sub>2</sub>=CF-(OCF<sub>2</sub>CFX) m-Oq-(CF<sub>2</sub>) n-A (inside of a formula m= 0-3, n= 0-12, q= 0 or 1, X=F or CF<sub>3</sub>, A= sulfonic-acid type functional group) can adopt preferably. The compound shown in \*\* 1 is mentioned as a desirable example of the above-mentioned fluoro vinyl compound.

[0012]

[Formula 1]

CF<sub>2</sub>=CFO(CF<sub>2</sub>)<sub>1-8</sub> SO<sub>2</sub> FCF<sub>2</sub>=CFOCF<sub>2</sub> CF(CF<sub>3</sub>) O(CF<sub>2</sub>)<sub>1-8</sub> SO<sub>2</sub> FCF<sub>2</sub>=CF(CF<sub>2</sub>)<sub>0-8</sub> SO<sub>2</sub> FCF<sub>2</sub>=CF(OCF<sub>2</sub> CF(CF<sub>3</sub>))<sub>1-5</sub> O(CF<sub>2</sub>)<sub>2</sub> SO<sub>2</sub> F. [0013] In addition, a perfluoro olefin like hexafluoropropylene, a chlorotrifluoroethylene, and perfluoro alkoxy vinyl ether can also be used instead of the above-mentioned tetrafluoroethylene which is the monomer which constitutes a fluorocarbon polymer.

[0014] The cation exchange membrane which consists of the above-mentioned perfluoro carbon polymer film can also be reinforced with a perfluoro carbon polymer the shape of a fibril, the shape of textile fabrics, and nonwoven blanket-like.

[0015] The cation exchange membrane of this invention sticks a gas diffusion electrode on the front face according to the usual known technique, subsequently attaches a charge collector, and is assembled as a fuel cell. Although a gas diffusion electrode consists of a sheet of the porosity object which made the conductive carbon black powder which made the platinum-catalyst particle usually support hold by hydrophobic resin binding material, such as a polytetrafluoroethylene (PTFE), it may contain the particle by which this porosity object was covered with the sulfonic-acid type perfluoro carbon polymer or this polymer. A gas diffusion electrode and a sulfonic-acid type perfluoro carbon polymer are stuck by the hot press method etc. The conductive carbon board with which the slot where a charge collector serves as a path of fuel gas or oxidizer gas was formed is used.

[0016]

[Example] Based on the method indicated by JP,2-88645,A, the ion-exchange-capacity 1.1 milliequivalent / g dryness resin which consists of a copolymer of CF<sub>2</sub>=CF<sub>2</sub> and CF<sub>2</sub>=CFOCF<sub>2</sub> CFCF<sub>3</sub> O(CF<sub>2</sub>)<sub>2</sub> SO<sub>2</sub> F were extruded at 220 degrees C, the film was produced, and the film with a thickness of 100 micrometers was obtained.

[0017] After hydrolyzing and rinsing the above-mentioned copolymer film in 30 % of the weight of dimethyl sulfoxide, and a 15 % of the weight [ of caustic potash ] mixed-water solution, it was immersed into the 1-N hydrochloric acid. Next, after rinsing the film and restraining the membranous neighborhood with an exclusive fixture, it dried for 1 hour and 60 degrees C of cation exchange membranes were manufactured. It was 8-ohmcm when the current-ratio resistance of this cation exchange membrane was measured.

[0018] The fuel cell property using this cation exchange membrane was evaluated. That is, PTFE was mixed in the carbon black powder which made the platinum-catalyst particle support, and the gas diffusion electrode of the shape of a sheet with a thickness of 250 micrometers was produced using the roll press. The membrane-electrode zygote was produced by inserting the above-mentioned cation exchange membrane and carrying out a laminating using a monotonous heat press machine between the gas diffusion electrodes of the two above-mentioned sheets. The amount of platinum catalysts of a membrane-electrode zygote is 2 1cm of film surface products. It was 1mg of hits.

[0019] Next, a membrane-electrode zygote is inserted from both sides in order of the charge collector made from titanium, the gas supply room made from PTFE, and a heater, and it is 2 9cm of effective film surface products. When the terminal voltage to the current density when having kept the temperature of the cell which finished setting up a fuel cell at 80 degrees C, supplying a positive electrode with oxygen and supplying hydrogen to a negative electrode with five atmospheric pressure, respectively was measured, it is current density 1 A/cm<sup>2</sup>. It was cell voltage 0.65V.

[0020]

[Comparative Example(s)] Based on the method indicated by JP,2-88645,A, the ion-exchange-capacity 1.0 milliequivalent / g dryness resin which consists of a copolymer of CF<sub>2</sub>=CF<sub>2</sub> and CF<sub>2</sub>=CFOCF<sub>2</sub> CFCF<sub>3</sub> O(CF<sub>2</sub>)<sub>2</sub> SO<sub>2</sub> F were extruded at 220 degrees C, the film was produced, and the film with a thickness of 100 micrometers was obtained. The same processing as an example was performed to this, and the cation exchange membrane was manufactured. The current-ratio resistance of this film was 12.6-ohmcm.

[0021] After finishing setting up a fuel cell by the same method as an example, when the terminal voltage to current density was measured under the same conditions, it is current density 1 A/cm<sup>2</sup>. It was cell voltage 0.60V.

[0022] The cation exchange membrane of an example has the small energy loss when finishing setting up a fuel cell compared with the film of the example of comparison so that the above-mentioned result may show.

[0023]

[Effect of the Invention] By making into a solid-state polyelectrolyte the cation exchange membrane which has the low electric resistance which is not in a film conventionally, a highly efficient solid-state polyelectrolyte type fuel cell is obtained.

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